MOLECULAR SIEVE CARBONS FOR GAS SEPARATIONS

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Introduction

Within the past 10 years, interest has grown in the separation, and capture of gases that are considered to be significant 'greenhouse' gases[1, 2, 3]. There is also growing interest in the capture of high-value gases from waste gas streams and in biogas upgrading requiring the separation and capture of CO_2 and H_2S from CH_4[4]. Molecular sieve carbons, either as adsorbents or as membranes, are being evaluated for each of these technologies. Many of these carbons are generated from pyrolyzed polymers. An early review of the diffusion of gases in molecular sieve materials was authored by Walker et. al.[5] and expanded in the classic work by Yang[6]. Yang identified five factors governing adsorber response in non-equilibrium gas separation systems: the equilibrium isotherm (major factor), resistances to heat and mass transfer between the bulk flow and the interior of the adsorbent particles, axial heat and mass dispersions, radial dispersions and variation of flow velocity in the adsorbent bed. Because the equilibrium isotherm is so important, acquiring isotherms through the use of a variety of probe adsorptives at different temperatures is believed to be an ideal way of characterizing molecular sieve carbons[7, 8]. The ability of a molecule to enter a slit-shaped pore in a molecular sieve carbon is dependent on the molecule's smallest diameter, referred to as MIN-1, withwater having the smallest MIN-1 at 0.29nm, and CO2 next at 0.32nm[9].

In 2005, ATMI commercialized a molecular sieve carbon generated from pyrolysis of a Saran polymer for storage of highly toxic gases used in the semiconductor industry. The work reported here describes adsorption studies on this commercial carbon and several new molecular sieve carbons using a range of molecules of differing sizes to characterize the porous structures of these carbons.
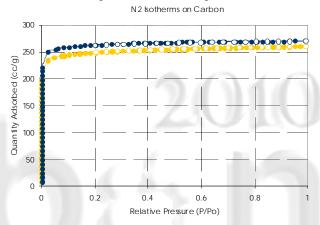
Experimental

Gaseous hydride adsorption measurements were obtained up to 0.1MPa pressure and at 294K using a modified Micromeritics ASAP 2405 porosimeter, with an Adixen MDP 5011 Molecular Drag Pump and 2005C1 Rotary Vane roughing pump vented to a Metron Tech. Novapure® S520 dry scrubber. N_2 isotherms at 77.4K and CO_2 at 273K up to 0.1MPa pressure were obtained via a Micromeritics ASAP 2420 using the microporosity analysis software.
Gaseous inorganic fluoride adsorption measurements up to 0.1MPa pressure and at 294K were obtained using a VTI Corp. GHP-300 Gravimetric Magnetic Suspension Balance and a gas delivery manifold with isolation valves actuated by a Honeywell MDA TLD-1 Toxic Gas Detector. High vacuum was from an Adixen turbo-molecular drag pump ATH31C backed by an ACP28G dry roughing pump each vented to an Metron Tech. Novapure® S451D dry scrubber. CCl_4 isotherms and single-point analyses were obtained using a gas manifold system and off-line weighing of gas cylinders.

Results and Discussion

The successful application of a molecular sieve carbon depends, very largely, on a complete understanding of its porous structure. While the measured values of 'equivalent surface areas' and micropore volumes are useful as a guide, micropore size distribution and pore-aperture size (or pore constriction size) are key elements. Unfortunately these are not easily obtained. Nitrogen adsorption isotherms and pore size information derived from those isotherms can be very misleading. In Fig. 1, N_2 isotherms at 77K are shown for two molecular sieve carbons and in Fig.2 CO_2 at 273K. DFT analyses are given in Fig. 3. The conclusion one might arrive at is that both samples exhibit similar porosities and should

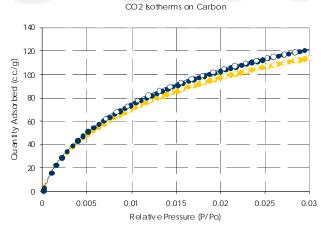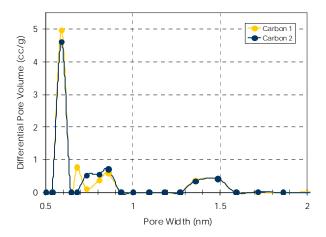**Fig.1** Nitrogen adsorption isotherms on two molecular sieve carbons: yellow – Carbon 1, blue, - Carbon 2.

Fig. 2 CO_2 isotherms on the same two carbons.

perform similarly in a sieving role subject to the molecular size of the species. In Fig. 4 isotherms are shown for the same two carbons but using the molecule neopentane, (0.62 nm kinetic diameter) adsorbed at 273K. Not only is there a major difference in pore volume between the two samples, but the

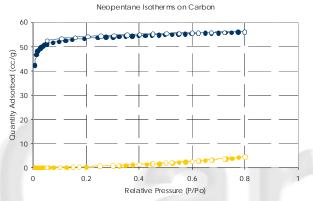**Fig. 3** DFT (N_2) analysis of the two carbons.

Fig. 4 Neopentane isotherms on the same two carbons.

Fig. 5. Porosity characterization using probe molecules.

volume for carbon 2, when computed as a liquid volume, is a full 70% of the micropore volume reported for nitrogen adsorption, implying that the porosity in Carbon 2 is mainly in slits of width greater than 0.62nm while that of Carbon 1 is all within slits much narrower than 0.62nm or is only accessed through slits of smaller width.

There are a variety of ways of post-treating MS carbon to refine its molecular sieving capability. Whichever technique is used to reduce the pore aperture/pore constriction size, the carbon may be viewed either as undergoing sintering or as receiving a layering of coke on the graphene walls. Both processes cause some diminution of total pore volume.

Adsorption isotherms have been obtained on a series of increasing post-treatment carbons using the following probe molecules: N_2(0.30nm), CO_2(0.32nm), AsH_3(0.38nm), i-C_4H_{10} (0.46nm), SF_6(0.49nm), CCl_4(0.57nm) and neopentane (0.62nm). The micropore volumes were measured using Dubinin-Ashtakov and α-S procedures and are reported, normalized to the pore volumes computed for AsH_3 in Fig. 5. What is significant is that the micropore volumes are high and similar for molecule access between 0.30 and 0.46nm size but, depending upon the degree of treatment, the access is restricted for molecules in the 0.46 – 0.62+nm size range.

Conclusions

Porosity analysis of molecular sieve carbons is enhanced by the measurement of adsorption isotherms using probe molecules varying in MIN-1 size. It is also evident that by careful adjustment of the processing conditions of the carbon, the porous structure can be modified to limit accessibility of molecules within a few hundredths of a nanometer.

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